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## CLAIMS

## [57] [Claim 1]

(1) An organic polymer which has a hydroxyl group or a hydrolytic basis combined with a silicon atom, and has at least one silicon content group which can construct a bridge by forming a siloxane bond, (2) Carbonylic acid calcium, carbonylic acid vanadate, carbonylic acid manganese, a hardenability constituent containing one or more sorts of carbonylic acid metal salt chosen from carbonylic acid nickel.

[Claim 2]

(1) The hardenability constituent according to claim 1 which becomes considering an amine compound as an essential ingredient as an ingredient.

[Claim 3]

(1) A number average molecular weight is within the limits of 500~50,000, and an organic polymer of an ingredient is a general formula to an end and/or a side chain of a main chain (1). :

[Formula 1]



the inside of a formula,  $R_1'$  and  $R_2'$  — respectively — independent — by the alkyl group of the carbon numbers 1~20. It is the Tori ORGANO siloxyl group shown by the alkyl group of the carbon numbers 0~20, the aryleyl group of the carbon numbers 7~20, or (R)  $\text{SiO}_2^-(\text{R}^2)$  is the substitution or the unsubstituted hydrocarbon group of the carbon numbers 1~20 independently, respectively. X is a hydroxyl group or a hydrolytic basis independent, respectively, a 0, 1, 2, or 3, 0, 1, or 2, and a b are not simultaneously set to 0, m is an integer of 0, or [-1~9]. The hardenability constituent according to claim 1 or 2, coming out and having one or more hydroxyl silyl groups per molecule expressed.

[Claim 4]

The hardenability constituent according to claim 3, wherein X is an alkoxyl group.

[Claim 5]

(1) A hardenability constituent given in any 1 paragraph of Claims 1~4 whose organic polymers of an ingredient are a polyoxyalkylene series polymer and/or a saturated hydrocarbon system polymer.

[Claim 6]

The hardenability constituent according to claim 5 which is a polymer, wherein said saturated hydrocarbon system polymer has a repeating unit consisting from isobutylene 50% of the weight or more in a total amount.

[Claim 7]

(1) Carbonylic acid calcium of an ingredient, carbonylic acid vanadate, carbonylic acid titanium, A, carbonylic acid barium, carbonylic acid manganese, and carbonylic acid nickel use as the main ingredients carbonylic acid metal salt expressed with general formula (2), (3), and (6) ~ (10).

respectively.  
Ca(OOCR)<sub>2</sub> (2)  
V(OOCR)<sub>3</sub> (3)  
Ti(OOCR)<sub>4</sub> (6)  
K(OOCR)<sub>7</sub> (7)  
Ba(OOCR)<sub>2</sub> (8)  
Me(OOCR)<sub>2</sub> (9)  
nickel(OOCR)<sub>2</sub> (10)

(The inside R of a formula is substitution or an unsubstituted hydrocarbon group, and may include a carbon carbon double bond.)  
[Claim 8]

(2) The hardenability constituent according to any one of claims 1 to 7 whose carbonylic acid metal salt of an ingredient is the carbonylic acid metal salt in which the melting point has an acid radical of carboxylic acid which is 65 °C or less.

[Claim 9]

(3) The hardenability constituent according to any one of claims 1 to 7 which is the carbonylic acid metal salt which has an acid radical of carbonylic acid whose carbon numbers in which carboxylic acid metal salt of an ingredient contains carbon of a carbonyl group are 2~17.

[Claim 10]

(4) A hardenability constituent given in any 1 paragraph of Claims 1~8 which are metal salt of a carbonylic acid group compound in which carbonylic acid metal salt of an ingredient is chosen from octanoic acid, 2-ethylhexanoic acid, neo-decanoic acid, oleic acid, or naphthenic acid.

[Claim 11]

(5) A hardenability constituent given in any 1 paragraph of Claims 1~10 containing the (B) ingredient of quantity which serves as 0.005 ~ 5 weight section by metallic element conversion contained in the (B) ingredient to ingredient 100 weight section.

[Claim 12]

(6) A hardenability constituent given in any 1 paragraph of Claims 2~10 containing the (B) ingredient of quantity which serves as 0.005 ~ 5 weight section by metallic element conversion contained in the (B) ingredient, the (C) ingredient 0.01 ~ 20 weight sections to ingredient 100 weight section.

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[Field of the invention]  
[00001] In this invention, it has the hydroxyl group or hydrolytic basis combined with the silicon atom, and a siloxane bond is formed. Therefore, it is related with the hydrophilicity constituent containing the organic polymer which has

[00002] [Description of the Prior Art] It is known that the organic polymer which contains at least one reactive silicon group in a molecule has the interesting character in which construct a bridge by formation of the siloxane bond.

[0003] In the polymer which it has, these reactive silicon groups polymer and a polysiloxane system polymer, is indicated by JP-S52-730988, A, JP-H5-252724, A, JP-H3-72627, A, JP-S63-60033, A, JP-S63-6041, A, JP-H1-33407, A, JP-H2-231758, A, etc.

produced industrially, and are widely used for uses, such as a sealing material, adhesives, and a paint.

especially the thing to excel in low moisture permeability and low gas permeability.

amine compounds, such as lauryl amine are used together as a co-catalyst in many cases for the polymerization of styrene.

the purpose of a silanol condensation catalyst, used to bridge construction and also accelerating a polymer which, on the other hand, has such a reactive silicon group, and also accelerating a condensation reaction. As such a silanol condensation catalyst, tin, such as octyltin (2-hexadecenoate acid) tin, The tin series catalysts represented by divalent tin, such as diethyltin bis(2-ethylhexanoate), is used widely, and when the movement of the tin which places especially a silanol on the hardend material, which has an acidity, is obtained many diene, tin

is used.  
[0007])

However, when octylic acid tin which is divalent tin, for example is used together with the amine compound of a co-catalyst and is used as a curing catalyst of the (A) ingredient, the intensity and elongation of a hardened material which are acquired may be insufficient, and an improvement of the

[0008] Although most is a dibutyltin type, the latter tetravalent tin series catalyst being used now. While the hardened material obtained has emollient, i.e., having a character to follow to the long-term stress change from the outside and fast curability, it is broadly used from the ability to apply as a curing catalyst of 1 liquid mold-curing nature constituent. However, since toxicity in case a small amount of tributyltin contains in this is regarded as a questionable, development of the silanol condensation catalyst of a non-tin series is desired.

[60000]

[0010] [Problem(s) to be Solved by the Invention] The purpose of this invention is as follows. Have practical hardenability and stability with a good hardened material obtained. Provide a hardenability constituent useful as the structural sealing material asked especially for high durability, the sealing material for multiple glass, the moisture seal material used for an electric device, and the like.

[0011] [Means for Solving the Problem]  
In order that the invention persons may solve such a problem as a result of incurring, as a curing catalyst of the (A) ingredient Carbonyl acid calcium, Carbonylic acid vanadium, carbonylic acid iron carbonyl aluminum, carbonylic acid potassium, by using one or more salts of carbonylic acid nickel, metal salt chosen from carbonylic acid cobalt, carbonylic acid manganese, carbonylic acid nickel, carbonylic acid cobalt, and carbonylic acid zinc, securing moderate hardness and stability, it finds out revealing high intensity and the physical properties of high elongation, compared with a

case where octenoic acid is used as a curing catalyst, and serve to complete the invention.

[0012] Namely, this polymer has a hydroxyl group or a hydroxide ion content group which can construct a bridge by forming a siloxane bond, (B), it is related with a hardenability constituent containing one or more tercaryls of carbonyloxy acid metal salt chosen from carbonyloxy acid calcium, carbonyloxy acid vanadium, carbonyloxy acid titanium, carbonyloxy acid potassium, carbonyloxy acid barium, carbonyloxy acid

[0013] An amine compound is related with the aforementioned hardenability constituent which becomes an essential ingredient as a (C) ingredient.

[0014] As a desirable embodiment, a number average molecular weight is within the limits of 500-50,000, an organic polymer of the (A) ingredient is a general formula to an end and/or a side chain of a main

10015

## Formula 2









end.  
[0075] As the vinylsilane which has a reactive silicon group, and vinylsilane, For example, vinyl trichlorosilane, vinyl methylchlorosilane, vinyldimethylchlorosilane, vinylchlorosilane, allyl methylchlorosilane, allyl dimethylchlorosilane, Allyl dimethyl methoxysilane, allyl diethoxy silane, diethoxy silane, gamma-methoxydi propyl trimethoxysilane, gamma methacryloyl oxypropyl methyl methoxysilane, etc. are used.

[0076] In this invention, a hydrogenation polybutadiene polymerization object which has a reactive silicon group can be mentioned as a saturated hydrocarbon system polymer which has a reactive silicon group. A hydrogenation polybutadiene polymerization object which has a reactive silicon group can be acquired by the hydrogenation reaction of a hydrogenation polybutadiene system polymer which has an end olefin group. General formula (17) after a hydrogenation polybutadiene system polymer which has an end olefin group uses a hydroxyl group as an end hydroxy hydrogenation polybutadiene system polymer as any metal groups, such as -ONa and -OK, first, for example :

Halogen atom, such as a chlorine atom, a bromine atom, and iodine atoms, and  $R^4$  are among [type 6, 7-9] and  $Y = -R^4-$ ,  $-R^5-$ ,  $-R^6-$ ,  $-R^7-$ ,  $-R^8-$ ,  $-R^9-$ ,  $-R^{10}-$ ,  $-R^{11}-$ ,  $-R^{12}-$ ,  $-R^{13}-$ ,  $-R^{14}-$ ,  $-R^{15}-$ ,  $-R^{16}-$ ,  $-R^{17}-$ ,  $-R^{18}-$ ,  $-R^{19}-$ ,  $-R^{20}-$ , and an alkylene group, a cyclo alkylene group, and an arylene group — it is desirable — by a divalent organic group shown. — It can obtain by making an organic halogenated compound shown by especially a divalent base chosen from  $CH_3^-$  and  $-R^1-R^2^-$ ,  $-CH_2^-$  and a hydroxide group of the carbon numbers 1-10) being preferred] react.

[0077] As a method of using terminal hydroxyl groups of an end hydroxy hydrogenation polybutadiene system polymer as a very metal group, A method of making it react to alkaliine water oxides, such as metal alkoxideNaOH the metal hydrideNaOCH<sub>3</sub> the Na and alkaline metalNaH like K and KOH, etc. is raised.

[0078] Although an end olefin hydrogenation polybutadiene system polymer used as a stretching material is obtained as an end hydroxy hydrogenation polybutadiene system polymer, a general formula (17) obtained in said method, Before making an organic halogenated compound of a general formula (17) react to obtain a polymer of the amount of Polymer Division molar, at the time, such as a methylene chloride, bis(chloromethyl)benzene, and bis(chloromethyl)ether, if it is made to react to an organic halogenated compound which can increase a molecular weight if it is made to react to a polyvinylidene halogenated compound which contains two or more halogen in one molecule, and is shown by a general formula (17), after that, A hydrogenation polybutadiene system polymer which is the amount of Polymer Division more, and has an olefin group at the end can be obtained.

[0079] As an example of an organic halogenated compound shown by general formula (17). For example, an allyl chloride, an allyl *s*-picture, vinyl(chloromethyl)benzene,  $A_1$   $M_1$  (chloromethyl) benzene,  $M_1$  (bromomethyl) benzene, Although allyl (chloromethyl) ether, allyl(chloromethyl) benzene, 1-butyyl (chloromethyl) ether, 1-ethoxy(chloromethyl) benzene, allyloxy(chloromethyl) benzene, etc. are reacted, it is not limited to them. Among these, an allyl chloride is cheap, and since it moreover reacts easily, it is desirable.

[0080] Introduction of a reactive silicon group to said end olefin hydrogenation polybutadiene system polymer may be manufactured by carrying out an addition reaction using a platinum system catalyst in a hydroxide compound like a case of an isobutylene system polymer which has a reactive silicon group in molecular chain terminals.

[0081] When a saturated hydrocarbon system polymer which has a reactive silicon group as mentioned above does not contain substantially an unsaturated bond which is not an aromatic ring is a molecule. Compared with a sealing agent etc. which consists of a conventional rubber system polymer like an

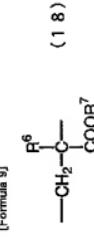
organic system polymer or an oxyalkylene system polymer which has an unsaturated bond, water resisting property is good remarkably. Since this polymer is a hydrocarbon system polymer, it is obtained.

[0082] An organic polymer which has these reactive silicon groups may be used alone, and may be used together or two or more sorts. Specifically, a polyoxyalkylene series polymer which has a reactive silicon group, a saturated hydrocarbon system polymer which has a reactive silicon group, a vinyl-base polymer which has a reactive silicon group, and an organic polymer which blends two or more sorts shown from a group, \*\* and others, can also be used.

[0083] A manufacturing method of an organic polymer which blends a polyoxyalkylene series polymer which has a reactive silicon group, and a vinyl-base polymer which has a reactive silicon group. Although indicated by JP 59-122341/A, JP 56-172831/A, JP 61-112624/A, JP 61-116763/A, etc. it is not limited to in particular these.

[0084] A desirable example has a reactive silicon group and a chain is as following general formula substantially (18) :

CH<sub>2</sub>—CH—Y—COOR<sup>7</sup> [0085] [Formula 9]



The acetoxy ester monomer unit which has an alkyl group of the carbon numbers 1-8 expressed with (a hydrogen atom or a methyl group, and R<sup>7</sup> show the alkyl group of the carbon numbers 1-8 among a formula, as for R<sup>6</sup>) (meto), and following general formula (19) :

CH<sub>2</sub>—CH—Y—COOR<sup>8</sup> [0086] [Formula 10]



(— inside of formula, and R<sup>8</sup> — the above — the same — R<sup>8</sup> shows with a carbon numbers of ten or more alkyl group —) — to the copolymer which consists of an acrylic ester monomer unit which has a with a carbon numbers of ten or more expressed alkyl group (meto), it is the method of blending and manufacturing the polyoxyalkylene series polymer which has a reactive silicon group. Acrylic acid (meta) expresses acrylic acid and/or metacrylic acid with the above-mentioned expressive form.

[0087] as R<sup>7</sup> of said general formula (18) — the carbon numbers 1-8 of a methyl group, an ethyl group, a propyl group, n-butyl group, a 2-ethylhexyl group etc. — desirable — 1-4 — an alkyl group of 1-2 is raised still more preferably. An alkyl group of R<sup>7</sup> may be independent and may be mixed two or more sorts.

[0088] as R<sup>8</sup> of said general formula (19) — ten or more carbon numbers of a lauryl group, a tridecyl group, a

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IP-4150220-B [DETAILED DESCRIPTION] 16/31 ページ

reacted and carboxylic acid metal salt which has the acid radical becomes a thing which has a high ionization potential or viscosity and which is hard to let (water-solubility) - bed. On the contrary, when a carbonaceous number of said carboxylic acid is small (a molecular weight is small), the ability of carboxylic acid metal salt may fall [carboxylic acid metal salt which has the acid radical], including especially an ingredient which volatilizes easily with heat. Especially on conditions [that layer] which is extended a constituent thinly, volatilization by heating may be large and catalysis ability of carbonaceous metal salt may fall greatly. Therefore, a as for said carboxylic acid, it is preferred that carbon

[010] Especially acquisition is easy and is cheap and a point that compatibility with the (A) ingredient is good to said carboxylic acid has 2-ethylhexanoic acid, oleic acid, neo-decanoic acid, oleic acid, or preferred naphthenic acid. Said naphthenic acid is expressed with an empirical formula (20).

[0103] 2-ethylhexanoic acid iron (IV) (avalemt) from a viewpoint of catalytic activity, 2-ethylhexanoic acid iron (IV) (avalemt), 2-ethylhexanoic acid titanium (tetravalence), neo decanoic acid iron (IV) (avalemt), Neo decanoic acid iron (IV) (avalemt), neo decanoic acid titanium (tetravalence), oleic acid iron (IV) (avalemt), Oleic acid iron (IV) (avalemt), oleic acid titanium (tetravalence), lauric acid iron (IV) (avalemt),  
Naphthalene acid iron (IV) (avalemt) and naphthalene acid titanium (tetravalence) are more preferred, and 2-ethylhexanoic acid iron (IV) (avalemt) and naphthalene acid iron (IV) (avalemt) are most preferred.

especially naphthenic acid ion (travalent) are present.

[0104] From a viewpoint of coloring to 2-ethylhexanoic acid and titanium (travalent), 2-ethylhexanoic acid, calcium (divalent), 2-ethylhexanoic acid potassium (univalent), 2-ethylhexanoic acid barium (divalent), 2-ethylhexanoic acid zirconium (travalent), Neo decanoic acid and titanium (travalent), neo decanoic acid calcium (divalent), Neo decanoic acid potassium (univalent), neo decanoic acid barium (divalent), a neo decanoic acid zirconium (travalent), Oleic acid and titanium (travalent), oleic acid calcium (divalent), oleic acid potassium (univalent), Oleic acid barium (univalent), an oleic acid naphthenic acid potassium (univalent), naphthenic acid titanium (travalent), calcium naphthenate (divalent), naphthenic acid barium (divalent), and a naphthenic acid potassium (univalent), naphthenic acid barium (divalent), and a naphthenic acid potassium (univalent), naphthenic acid barium (divalent), and a naphthenic acid

[0107] with a restraint on whose metal content is about 1 to 40 g of urethane.

workpiece except a good hardened material in a workpiece, generation of (B) ingredient exceed this range. The time of hardening arises, and it is hard to be obtained. If loadings of the (B) ingredient exceed this range, the aforementioned carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid manganese, carboxylic acid cobalt, and carboxylic acid zirconium. Besides

using it alone, it can be used combining two or more sorts, and also can use together with carbonic acid salt, carbonic acid lead salt, carbonic acid bismuth salt, carbonic acid cetic salt, etc.

[0108]

On the other hand, only with carboxylic acid metal salt of the (B) ingredient activity is low, and when moderate hardenability is not acquired, various amine compounds which are the (C) ingredients as co-catalyst can be added. As various amine compounds, although indicated to JIS-B-2617/1A, for example, Specifically Methamine, ethylamine, propylamine, isopropylamine, *n*-butylamine, amylamine/amine, etc.

thus, or more pieces are scattered

[0113] As these (C) ingredients, since co-catalyst ability changes greatly with structure of the (C) ingredient, it is preferred to choose a compound which was compatible, or at least compatible, with the (A) ingredient to be used. For example, when using an isobutylene/alkene copolymer as a (A) ingredient, aliphatic series secondary amines, such as *tert*-butylamine, are preferred among aliphatic series secondary amines, such as diethyl amine and diethylbenzylamine, are preferred from a point that co-catalyst ability is high.

[0114] Silane coupling agents other than an amino group content silane coupling agent can also be used for a coupling of this invention.

[0115] An *alkylsilane* other than an *aminosilane*, a *substituted aminosilane* or an *anhydrosilane*.

chloropyromesane, L such as tris (trichloromethyl)benzene, gamma-isocyanatoisocyanate, isocyanatoisocyanate, gamma-isocyanatoisopropyl triethoxysilane, gamma-isocyanato propylmethoxy silane, and gamma-isocyanato propylmethoxy silane, silanizing agent, etc, which are the derivatives which denaturized these can be used as a silane coupling agent.

silane coupling agent J has  $\text{WFI} = 20$  preferred weight section to  $\text{WFI}$  current  $\text{WFI}$  weight section;

and also its  $0.1 = 5$  weight fraction is more preferred

0119

In a hardening or a lot of building, constituents of this invention, since a elongation of a hardened material can be gained if a plasticizer is used, using it together with a building agent, it is more effective. As an example of a plasticizer, diocyl phthalate, dibutyl phthalate, dibutyl phthalate ester, such as butylbenzyl phthalate, di-*tert*-butyl phthalate, and JISD undexyphthalate. Diethyl adipate, \*\*\* aliphatic diacid ester, such as a succinic acid seocid and diocyl seobutyrate. Diethylene glycol dibenzoate, \*\*\* aliphatic diacid ester, such as a pentadecylic ester. Butyl oleate, behenate, Diethylene glycol dibenzoate, \*\*\* aliphatic diacid ester, such as methyl acetyl ricinoleate. Tridecyl phosphate, \*\*\* seobutyrate. Diethylene glycol dibenzoate, and ethoxybenzoate, and chloroethyl octadecylbenzoate. Enclosed sohd \*\*\* aliphatic series ester species, such as methyl acetyl ricinoleate, and epoxy stearic acid benzyl Polyesters, and epoxy stearic acid, such as epoxidized linseed oil and epoxy stearic acid benzyl Polyesters, such as a polyesters bisacrylate, [Poly (alpha-methylstyrene),] Polyacrylate, such as polyacrylene, Polybutadiene, Acrylonitrile, polychloroprene, polyisoprene, polybutene, hydrogenation polyisoprene, Hydrocarbon system oligomers, such as a process oil.

chlorinated paraffins are illustrated.

## IB 4150220 B [DETAILED DESCRIPTION]

[0125] An epoxy resin receives reactive-silicon-group-containing-organic-polymer 100 weight section. It is preferred to use it in the range of one to 100 weight section and also ten to 50 weight section, and is preferred to blend a hardening agent of an epoxy resin per epoxy resin 100 weight section in the range of one to 200 weight section and also ten to 100 weight section.

[0126] An inordinate which limitation in particular does not have in the method of preparation of a hardener/hardening agent of this invention, for example, was described above is blended, it needs to be hardened ordinary temperature or heating using a mixer, a roll, kneader, etc., or an ingredient is dissolved in a suitable solvents, and a usual method of mixing or making is used. A 1:1 liquid/solvent ratio, a two-component type, or many liquid type compound can also be built and used by combining

[0122] In a hardenable composition of this invention, various additive agents can be added if needed. Other occurring catalysts as an example of said additive for example, tetravalent tin, divalent tin, divalent lead, etc. Adhesive grant agent which adjust the rheological characteristics of hardened material to generate, such as physical- $\rightarrow$  properties regulator and a shear coupling agent. An antioxidant, radicales scavenger, and a stabilizer, etc. In a hardenable composition of this invention, various additive agents can be added if needed. Other occurring catalysts as an example of said additive for example, tetravalent tin, divalent tin, divalent lead, etc. Adhesive grant agent which adjust the rheological characteristics of hardened material to generate, such as physical- $\rightarrow$  properties regulator and a shear coupling agent. An antioxidant, radicales scavenger, and a stabilizer, etc. [0123]

Since a hardening constituent of this invention has outstanding weatherability, heat resistance, and water resistance, and electric insulation resulting from a principal chain skeleton and it has high intensity and a physical-properties improvement effect of high elongation. It can use conveniently for electrical insulation materials, such as electric electronic component materials, such as a structural elastic sealing compound, a sealing material for mobile glass, a solar car rear-face binder, a binder adhesive, a paint, infusible resin, a material for a cable, a binder adhesive, a paint, infusible resin, a material for a wire, material for an electric wire, a sealing agent for water prevention, a water proof, etc. It is useful especially when used as a coating material, a coating agent for rust prevention, a water proof, etc.

[0131] [Example] Although working example and a comparative example explain this invention concretely below, this invention is not limited to this.

Identifiers: Petrobenzol [1], trade name PA5000A 80 weight section, Colloid calcium carbonate (Maruo Calcium Co., Ltd. make, trade name SHIRETTSU 50/50 weight section, Colloid calcium carbonate (Maruo Calcium Co., Ltd. make, trade name MC-50) 50 weight section, Heavy calcium carbonate (product 1 made from Shiroishi Calcium 1 trade name SOUTON 3200) 40 weight section, Photo-catching resin (Toagosei make, trade name ARONKUSU M-309) 3 weight section, Benzoylbenzoyl system ultraviolet ray absorber (Giese Giese Japan make, trade name SANRUI LS-770) 1 weight section, Hindered amine light stabilizer (Sanryo Co. Ltd. make, trade name IRUGA NDx 1 weight section, hindered phenolic antioxidant (Ciba-Geigy Japan make, trade name IRUGA NDx with 0.3 weight section, and water 5 weight section were measured respectively, and it often irritated

[111-112] next — as the (B) ingredient — octyl acid (2-ethylhexanoic acid) calcium salt (the Nihon Kagaku Sangyo Co., Ltd. make). The trade name NIKKAKU Chicks Ca 8% toluene solution was used as a hardening agent. Lin / for the thing for which dietary amine (the Kao Corp. make, Firmin D86) was shown in Table 1 as a (C) ingredient and which could number/ of weight sections /-

[0133] measure, could use the spatula, and was stirred and mixed / working example - 1

Sanyo Co., Ltd make) as a trade name NIKKANAFU textile V 26 toluene solution and the (C) ingredient — diethanol amine (the Kao Com make). The number of weight sections [—used thing

I used this which shows lauryl amine in Table 1 respectively and the Japanese east transformation Make, trade name neo SULTAN U-28 and a (C) ingredient was made into the comparative example 1.

In accordance with the terms contained in method of 5758 - 1982 N of JIS, the examination was performed with H type sample container by the above-mentioned method on condition of speed of testing 50 mm/min around 23 °C and the thermoelectric chamber of 50±5% of humidity.

The recovery was measured by the following method. First, after making a H type sample which ended up being 100 mm wide for one day and taking it out, the above-mentioned care of health informed me that water for one day, after having compressed and fixed to 70 so that sample thickness might be 12.84 mm, and heating a sample in 100 °C air-drying equipment for one day, it released from compression and was neglected under the room temperature on the 1st. The thickness of sample in this case was measured and the recovery to

Time (leather-covered time) until it fills the same compound in an ointment can simultaneously as a compressed part was computed.

measure which estimates hardenability and stretches a hide on the surface under 23 °C and the

conditions of 50% of relative humidity was measured. The one where leather-covered time is shorter shows that hardenability is high.

[0138] A result is shown in Table 1. The filled hardened material is that cohesive failure is shown, and CF showing the fracture state in front is a fracture state which can be searched for as a sealing material.

[Table 1]

		実施例1 実施例2 実施例3 実施例4 比較例1				
(A) 成分		EP505S	phr		150	
PA05004	phr			60		
シリコン2200	phr			50		
シリコン3200	phr			40		
MC-5	phr			50		
エレコト828	phr			5		
アクリルAM-309	phr			3		
イソブリクタノ1010	phr			1		
カゼイ-327	phr			1		
サル-MLS-770	phr			1		
水	phr			5		
(B) 成分						
カチル酸Ca	phr	5.7				
ナフチル酸V	phr			60		
カチル酸Fe	phr			50		
カチル酸Ti	phr			40		
カチル酸Sn	phr			30		
(C) 成分						
シリコーンシリコン	phr	0.74	0.74			
カチルアミン	phr			1.00	0.26	0.66
硬化性 剤		皮膜引張時間	時間	4	4	4
H型引張特性		破断強度	MPa	0.05	0.07	0.08
		破断伸び	%	0.45	0.64	0.27
		破壊状態	CF	770	760	440
		復元率	%	57	73	27

Using an isobutylene system polymer as an ingredient (A) as shown in Table 1 as a (B) ingredient, when diisobutylene amine and silyl amine were used together for octyl acid calcium, naphthalene acid

covered time about 40 minutes was measured. The one where leather-covered time is shorter shows that hardenability is high.

[0139] A result is shown in Table 1. The filled hardened material is that cohesive failure is shown, and CF showing the fracture state in front is a fracture state which can be searched for as a sealing material.

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Since an adhesive property turned into the important characteristic as a liquid mold-curing nature constituent, the adhesive property was checked using anodized aluminum and a vinyl chloride steel

covered time about 40 minutes was measured. The one where leather-covered time is shorter shows that hardenability is high.

[0140] A result is shown in Table 1. The filled hardened material is that cohesive failure is shown, and CF showing the fracture state in front is a fracture state which can be searched for as a sealing material.

<http://www4.ipdl.inpit.go.jp/cgi-bin/tran.web.cgi?u=http%3A%2F%2Fwww4.ipdl...> 2010/05/06

**Plalets.** On each substrate which purified the surface by methyl ethyl ketone, 1 liquid mold-curing monomer constituent was placed from 1 liquid cartridge using commercial dispenser to the cross shape  $1 \text{ mm} \times 1 \text{ mm}$  length of about 1 cm, and it was cured for 23 sec.  $140 \pm 10^\circ\text{C}$  for 14 days per day. The manual friction test was done after care of health, cutting an adhesion side deeply with a cutter knife, and the surface of this substrate was observed. The liquid hardened material is that extremely failure is shown, and CF in Table 2 is a fracture state searched for as a sealing material.

investigated.  
[0144]

A result is shown in Table 2. [9145]

[Table 2]

配合表	成分	製品名	実験例1	比較例2	
	(A)成分	S203	95	95	重量部
	PPG3000	55	55	重量部	
	白炭酸CCP	120	120	重量部	
	光安定剤	サノールLS-770	1	1	重量部
	紫外線吸収剤	チミド <sup>®</sup> 327	1	1	重量部
	タリス <sup>®</sup> 止剝	ディスクロン <sup>®</sup> 6500	2	2	重量部
	硬化チタン	タイペークR-B20	20	20	重量部
	脱水剤	A-171	2	2	重量部
	接着性付与剤	A-1120	3	3	重量部
(B)成分	オクタメチルコニウム	8.1			重量部
	U-220			2	重量部
(C)成分	ラウリルアミン	1.4			重量部
H型引張機械特性	M50	0.27	0.19	0.19	MPa
	M100	0.38	0.31	0.31	MPa
	M150	0.48	0.40	0.40	MPa
	TBL(破断強度)	0.64	0.93	0.93	MPa
	EB(延伸伸び)	520	570	570	%
接着性	接着強化アルミニウム	CF	CF	CF	接着強化状態
	塗 <sup>®</sup> 鋼鐵	CF	CF	CF	接着強化状態
硬化性	底部硬化性	23°C×1週間 23°C×2週間	7.7 12.2	10.6 15.6	mm mm
	深部硬化性	23°C×1週間 23°C×2週間	7.2 12.0	10.8 16.4	mm mm
防錆安定性 (50°C×2週間貯蔵)					

As opposed to the polyether system polymer which serves as the (A) ingredient in our invention example 5, (B) vinyl in the laurylamine, which acts the carboxylic acid/zirconium salt which acts as a co-catalyst as a (C) ingredient further as a silanol condensation catalyst as an ingredient. Although hydrolytic stability was slightly inferior as compared with the comparative example 2 using although hydrolytic stability was terminated in catalyst, almost comparable elongation and an adhesive property were revealed and it showed that 1 mol-% mol-curing-temperature constituent which is polypropylene was obtained (Table 21) (Synthetic example 1).

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http://www.indiainfo.in/cgi-bin/tran\_web.cgi?u=http%3A%2F%2Fwww4.ipd.i... 2010/05/01

polyisoprene oxide was obtained. Then, the methanol solution of NaOMe of the equivalent amount was added to the hydroxyl group of this polyisoprene oxide, and after the addition of methanol was distilled off, and also the allyl chloride was added, and the hydroxyl group of the allyl group was changed into the silyl group. By the above, the end obtained 3 organic-functions polyisoprenylpropylene oxide of the number average molecular weight 20,000 [about] which is an allyl group.

following compo  
[0147]

(A)

Next, the residing pressure glass liquified gas extraction pipe with a needle valve containing 438 ml (5.15 g/mol) of isobutylene monomers was connected to the three-way cock, and after attaching the polymerization vessel over dry  $\text{O}_2$  - ethanol bus of  $-70^\circ\text{C}$  and cooling, the inside of a container was made decompression using the vacuum pump. After opening the needle valves and introducing of an isobutylene monomer in a polymerization vessel as extraction pipe, the inside of a container was returned to ordinary pressure by introducing nitrogen from one side in a three-way cock. Next, 0.72 g (7.7 mmol) of 2-methylpyridine was added. Next, 0.55 ml (5.63 mmol) of  $\text{FeCl}_3$  - tetrachloroethane was added, and the polymerization was started. 10 minutes after the polymerization start, 720  $\mu\text{l}$  (6.3 mmol) of allyl trimethylsilane was added, and the initiation reaction of the allyl water washed [1, 20 minutes] the reaction solution 4 times, the allyl and isobutylene system polymer

[0148]

[0149] 2.1 [PS-1] is the isotobylene system polymer and plasticizer which have a reactive siloxane group in the both ends of the target chain of the mixtures (A-2) of the weight ratio were obtained. In this way, if the obtained polymer is measured by the GPC method (it was considered as the (Iu) sample system and, for the solvent, the column used  $\text{HCl}_3$  using Shodex K-304 taurin LCM-800 (made from Waters)), the number average molecular weight was 1,040 and  $M_w/M_n$  (ratio of weight average molecular weight to a number average molecular weight) was 1.23.  $^{13}\text{C}$ -NMR (using Varian Gemini200) The proton which belongs to each structure by measurement of polymer-term or initiator origin (6.75 ppm) The methyl proton combined with the silicon atom of polymer-term origin. As a result of measuring and measuring the intensity of  $\text{O}-\text{Si}-\text{O}$  1 ppm and the resonance intensity of methoxy protons 4.35, the end (i) functional group number Fri (number of the allyl group per one molecule of isotobylene polymer) was 1.76. (Working example 8-1, comparative example 3)

[1515] Next, as a (B) ingredient, which is a sialic condensation catalyst, lauryl amine was further measured to the various carboxylic acid metal salt shown in Table 1 to the above mentioned base metal as for (C) ingredient, the spatula was used for it, and it stirred and mixed for 3 minutes. It was made for the numbers of the metal ion containing the number of addition parts of the various carboxylic acid metal salt of the (B) ingredient to become the same here. The mold about 3 mm

[0152] The combination presentation of base resin, a curing catalyst, etc. and the physical-properties evaluation result of the hardened material obtained from it are shown in Table 3.  
[0153]

[Table 3]



When the various carboxylic acid metal salt of working example 16-28 is used as shown in Table 4, in spite of having used the silanol condensation catalyst of the non-bin series, the surface has hardened in five days.

Practical hardenability was shown.

On the other hand, when the carboxylic acid zinc of the comparative example 4 was used,

hardenability had not hardened five days after test.

[0157] As mentioned above, the organic polymer which has at least one reactive silicon group in the (A) molecule, (B) carboxylic acid and calcium, carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, one or more sorts of carboxylic acid metal salt chosen from a carboxylic acid zirconium, and a hardenability [\*\*\* and others] constituent. In spite of being a non-bin series catalyst, practical hardenability is shown, and it turns out that hardened material physical properties are also fine (high elongation and high intensity).

(Comparing using the trimethoxysilyl group as a reactive silicon group).

If a trimethoxysilyl group useses polyacrylates series polymer which exists in molecular chain terminals as a reactive silicon group, cure rate will become large from the polymer of the synthetic example 1. The direction of a trimethoxysilyl group of that is because reactivity is larger than a methyl trimethoxysilyl group. Such a polymer is indicated to JP 2011-172804 or JP 2011-27855 A. For example, the same hardenability constituent as working example 6-15 can be prepared using the polymer indicated for the example 1 of manufacture JP 2011-172804 A. The task free time of this constituent is shorter than working example 6-15. The same hardenability constituent as working example 6-15 can be prepared using the polymer indicated for the example 1-4 of manufacture of JP 2011-27855 A. The task free time of this constituent is shorter than working example 6-15. Therefore, a catalyst amount can be lessened. If cure time is made into the same grade, and the polymer which has the above-mentioned trimethoxysilyl group will be used.

[0158] If the mixture of the polymer which has a trimethoxysilyl group, and the polymer which has a methyl dimethoxysilyl group is used as a polymer, cure time and the physical properties of a hardened material are freely controllable. For example, the hardenability constituent of working example 6-15 can be prepared using the polymer which mixed the polymer which has a trimethoxysilyl group, and the polymer which has a methyl dimethoxysilyl group by the weight ratio of 1:10-10:1.

[0159] Working example when the polymer which has a trimethoxysilyl group is used is shown below.

(Synthetic example 3) The inside of bottom of  $N_2$  atmosphere 1L autoclave. According to a composite metal complex compound catalyst. It polymerizes the obtained polypropylene oxide. Use and to the compound number average molecular weight 7,000 and the polypropylene oxide [1000g of molecular-weight-distribution  $M_w/M_n=20$ ] as 19g of gamma-isobutylene propyltrimethoxysilylamine [Nippon Unicar make Y-5187] and a catalyst, 0.05 g of diethyl tin screw isobutylene propyltrimethoxysilylamine [made in U-360] transformation [Japanese east 1] is added. It reacted at 90 °C until the isocyanate group was no longer detected in IR under the nitrogen air current in this, and the reactive silicon group content polypropylene (6-3) when the trimethoxysilyl group was introduced into about 80% of ends was obtained (Working example 6-2).

(A) The polyoxalkylene series polymer (A-1) which has as an ingredient, the methyl dimethoxysilyl group obtained in the synthetic example 1. The various carboxylic acid metal salt which is the (B) ingredients according to the formula shown in Table 5 using the polyoxalkylene series polymer (A-3) which has the trimethoxysilyl group obtained in the synthetic example 3, (C) Lauryl amine which is an ingredient it was measured, respectively, the statula was used, and it stirred and mixed for 30 seconds. It was made for all the numbers of the metal atom containing the number of addition parts of the various carboxylic acid metal salt of (B) ingredient to become the same. Here, The surfaces was lightly pressed down with the statula after mixing, and time (lauster-covered time) until a constituent stops adhering at the tip of a spatula was measured.

[0160] An evaluation result is shown in Table 5.

[0161] [Table 5]

(1) : 2-エチルヘキサン酸鉄のミネラルスピリット溶液、金属(Fe) 含有量: 6 %  
 (2) : 2-エチルヘキサン酸カルシウムのミネラルスピリット溶液、金属(Ca) 含有量: 5 %

(A) 成分	組成(重量部)		実施例			
	A-1	A-3	29	30	31	32
(B) 成分	ニッカオテックス鉄6% (T) <sup>(1)</sup>	日本化学産業(株)	100	100	100	
	ニッカオテックスカルシウム6% (T) <sup>(2)</sup>	日本化学産業(株)		6.6	6.6	5.6
(C) 成分	ラウリルアミン		0.66	0.66	0.66	0.66
	皮張り時間(23°C)		41min	21min	300min以上	105min

As shown in Table 5, the polyoxalkylene series polymer (A-3, working example 30 and 32) which has a trimethoxysilyl group had the cure rate quicker than the polyoxalkylene series polymer (A-1:

working example 29 and 31) which has a methyl dimethoxy silyl group.

[0162] The same hardenability constituent as working example 6-15 can be prepared using the polyacrylic acid series polymer (A-3) which has the trimethoxysilyl group obtained in the synthetic example 3. The tack free time of this constituent has short cure time, and good physical properties are acquired.

(Constituent which used the epoxy resin together)

The same hardenability constituent as working example 6-15 can be prepared using the constituent which used together reactive silicon group containing organic polymer and an epoxy resin. When this constituent is used, the manifestation of adhesive strength is quick.

[0163]

[Effect of the invention]

(A) The organic polymer which has the hydroxyl group or hydrolytic basis combined with the silicon atom, and has at least one silicon content group which can construct a bridge by forming siloxane bond, (B) Carboxylic acid dodecanoic acid, carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium. The hardenability constituent containing one or more sorts of carboxylic acid metal salt which it comes to choose out of carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium. While revealing practical hardenability and stability, the hardened material obtained shows the outstanding mechanical physical property which has high intensity and high elongation as compared with the case where the carboxylic acid tin currently used conventionally is used as a curing catalyst. Therefore, the hardenability constituent of this invention is very useful as various elastomers, such as a sealing material, adhesive, a binder.

[Translation done.]